SURFACE TREATING METHOD

FIELD OF THE INVENTION

The present invention relates to a surface treating method and, more particularly, it relates to a surface treating method having little load to environment.

BACKGROUND OF THE INVENTION

In recent years, the regulatory environment in all aspects of ESH (ESH: Environment, Safety and Health) in a global scale has been highlighted. Incidentally, the term "regulatory environment" used here is essentially different from the problem such as pollution that is relatively local and within an ability of cleaning up by the earth itself but needs a countermeasure in a global scale.

In a semiconductor industry, environmental management is important as well and, at present, it is most important matter that it reduces exhaustion of PFC (perfluorocarbon). In the semiconductor industry however, the matter to be solved concerning the environmental problem is not only the above but also reducing and recycling waste of acid and organic solvents and reducing consumption of electric power.

In a manufacturing process of semiconductor devices, cleaning of various contaminations of semiconductor wafers have

been carried out by a method where the wafer is dipped in acidic or alkaline solution such as a mixed solution of sulfuric acid/hydrogen peroxide, a mixed solution of hydrochloric acid/hydrogen peroxide and a mixed solution of ammonia/hydrogen peroxide and then heated or applying with an ultrasonic vibration. For example, removal of metal contamination adhered on the surface of wafer is carried out by oxidation (ionization) of metal using sulfuric acid or the like so that the contamination is eluted into a solvent to make into a solvated (hydrated) ion for stabilization.

However, when the waste resulted by such a cleaning treatment is made nontoxic, waste such as sludge is produced. In addition, the amount of the waste liquid produced by the above cleaning treatment is huge and, further, a lot of electric power and water are necessary for treating that. Therefore, cleaning using sulfuric acid or the like has a very big environmental load.

Because of those reasons, it has been preferable that a solvent for a solution for cleaning of wafers is water. it has been also preferable to use a solution containing no element other than H and O such as pure water and hydrogen peroxide solution instead of acidic or alkaline solution. Thus, for removal of metal contaminations, it is ideal that metal is efficiently ionized using H_2O, H_2O_2 or the like and is removed as a hydrated ion. For removal of organic contaminations and

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particles, it is ideal that the organic substance is oxidized and decomposed using H_2O, H_2O_2 or the like.

As such, the cleaning treatment using H_2O, H_2O_2 or the like is very effective in view of the waste management. On the contrary however, huge electric power is needed to purify the feed water. Therefore, it has been demanded to reduce the amount of pure water used in the rinse processes. Thus, it has been briskly demanded to develop a dry cleaning technique as a substitute for a conventional liquid phase cleaning technique.

Among the cleaning treatment of organic substances, removing resist needs the largest amount of chemical solution and, further since it is a liquid phase heating treatment, electricity consumption is relatively high and it is large loading to air-conditioning equipment for clean rooms as well. Therefore, various alternatives processes have been studied and, as one of them, a process to remove resist using aqueous ozone of high concentration has been investigated.

Since aqueous ozone consists of O_3 and H_2O only, treatment using that is very effective to reduce the environmental load from a viewpoint of waste management. However, in this process, to achieve a desired throughput is difficult due to the following reasons.

In a resist removing process using aqueous ozone, the removal rate is proportional to the concentration of ozone.

Accordingly, in order to make the ozone concentration high for increasing the removal rate, it is necessary to lower the temperature of the aqueous ozone. However, when the temperature of the aqueous ozone is lowered, the reaction rate decreases. Therefore, in the above process, there is an upper limit for the resist removal rate.

In addition, the treatment using ozone has another problem. For example, ozone is explosively decomposed into oxygen and, therefore, its handling is to be careful. As to another cleaning technique utilizing the high oxidizing ability of aqueous ozone, a spin cleaning method of a single-wafer type where an aqueous ozone and diluted hydrofluoric acid are alternately supplied to a wafer has been known. Another method where hydrogen peroxide or ammonia is added to an aqueous ozone and then ultrasonic wave of an MHz region is applied to promote the production of OH radical in the liquid and it cleans out by improving the oxidative ability of the liquid by the OH radical produced by that has been known as well. However, in any of those methods, ozone is used and, therefore, the above-mentioned disadvantage is not overcome yet.

With regard to a cleaning method using no ozone, a method where ultrasonic wave of an MHz region is applied to dissolved aqueous oxygen or dissolved aqueous hydrogen has been reported. This method also intends to improve the oxidative ability by promoting the production of OH radical in the liquid. Since

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the dissolved aqueous oxygen and dissolved aqueous hydrogen used in this method are relatively safe, there is no need for being careful as in the case of using ozone. However, when dissolved aqueous oxygen is used, there is an upper limit for the dissolved oxygen concentration. In addition, when dissolved aqueous hydrogen is used, there is a disadvantage that the hydrogen concentration margin for an optimum cleaning effect is narrow owing to competitive reaction between OH radical formation and OH radical deactivation by H radical.

As a method for cleaning a semiconductor wafer, Japanese Patent Laid-Open Nos. 7869/1993 and 137704/1998 disclose a method using a highly functional cleaning solution prepared by applying microwave to a chemicals solution.

Japanese Patent Laid-Open 7869/1993 disclose a method that microwave is irradiated to pure water which is contacting to a catalyst consisting of palladium or platinum powder and the pure water where a wetting property becomes high is supplied to a use point for cleaning. However, although the microwave excitation lifetime of pure water in a liquid phase is not more than several milliseconds, the pure water irradiated with microwave in this method is supplied to the use point after passing through a pipe and then filtered. Therefore, it is likely that the effect of microwave excitation is lost at the use point already.

In order to improve that, Japanese Patent Laid-Open No.

137704/1998 discloses a direct irradiation of microwave to the cleaning vessel. According to this method, microwave's irradiation excites pure water or cleaning solution and the molecular group constituting that is cleaved into small size. As a result, surface tension of pure water and cleaning agent solution at the wafer surface becomes lower and wetting increases and radicals are generated and, therefore, a cleaning solution having a high chemical reactivity can be permeated into the inner side of the fine pores. In addition, since the liquid temperature can be raised uniformly and within short time by an induced heating effect, a high reaction rate can be achieved. However, even in this method, large amount of pure water is still consumed for the cleaning and huge electric power is needed for its production.

Environmental problems concerning the cleaning treatment of semiconductor wafers was explained hereinabove and, as will be mentioned below, there are same problems in other treatments as well.

For producing relatively thin silicon oxide film and metal oxide film used as gate insulating film or capacitor, or for etching semiconductor film, metal film or insulating film, it has been used oxide species having a relatively strong oxidizing ability such as oxygen, ozone, dinitrogen monoxide and nitrogen monoxide. Making the film thinner and the line width smaller will be more and more carried out in future and, in order to

achieve that together with film quality of less defects, it is important that the oxidizing species are not supplied solely but both oxidants and reductants are simultaneously supplied to control the reaction rate. For example, in the case of carrying out the heating treatment of wafer where metal such as tungsten is exposed, it has been adopted a method where partial pressure ratio of oxygen to steam is regulated so that oxidation of tungsten is prevented.

Usually, such treatments except etching are carried out in a heat-treating furnace such as an electric furnace or an infrared heating furnace. However, in the furnace, thermal efficiency is poor and consumption of electric power is high whereby environmental load is very big.

Further, in every treatment, the use of gases which may cause an ozone depletion and/or the so-called global warming gas having very big global warming potential (GWP) as a supplying gas and an exhausted gas is to be avoided. The global warming potential is a product of the lifetime of the used gas in air (which is mostly determined by the reaction rate with OH radical) and the infrared absorption coefficient of the said gas at the air window region (an infrared region of about 8-13 μm wave length except the infrared absorption band derived from H_2O). Thus, it is not recommended to use the gas having absorption band in the region except the infrared absorption band derived from H_2O as a supplying gas and/or an exhausted gas.

As mentioned above, although cleaning with acid or alkali is effective for removing metal contaminations, organic contaminations or particles, those need a waste liquid processing step having a big environmental load. In a cleaning method using aqueous ozone or a cleaning method using oxygen-dissolved water or hydrogen-dissolved water which has been started in practical use as a substituted method therefor, solubility of such gases in water is several tens ppm at best and, therefore, concentration of the resulting oxidizing species is limited by the solubility whereby it is difficult to achieve a sufficient throughput. In addition, in a cleaning process of liquid phase including a pure water rinse and a spin cleaning method of a single-wafer type, large amount of pure water is used as a reaction species or solvent and, therefore, an equipment for purifying the feed water in large scale having a big environmental load is necessary. Thus, each and any of the above-mentioned surface treating methods dose not have a small environmental load and does not have a high treating ability.

SUMMARY OF THE INVENTION

The present invention has been accomplished in view of the above circumstances and its object is to provide a surface treating method having a small environmental load.

Another object of the present invention is to provide

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a surface treating method whereby a surface treating is made possible by a sufficient throughput.

Still another object of the present invention is to provide a surface treating method whereby a surface treating is possible without the use of large amount of pure water.

In order to solve the above-mentioned problems, the present invention provides a surface treating method, treating the surface of a member, comprises;

producing a cluster having the first molecule and the second molecule bonded together by an inter molecular force in a gas phase, making the first molecule more reactive than the first molecule in case of not bonded with the second molecule by using at least a part of internal energy released in producing the cluster; and

treating the surface of the member in a gas phase with the cluster containing the first molecule made in a state of higher reactivity.

It is preferable that the first molecule and the second molecule are different.

It is preferable that the second molecule acts as a catalyst to make the first molecule higher reactivity.

It is preferable that the first molecule is hydrogen peroxide molecule while the second molecule is water molecule.

It is preferable that the first molecule in higher reactivity contains oxywater.

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It is preferable that the first molecule and the second molecule are supplied so that their molar ratio near the surface of the surface of the member is made 1:3.

It is preferable that electromagnetic field is irradiated to the cluster in producing the cluster.

It is preferable that the energy of the electromagnetic field is 0.4 eV or more.

Making the first molecule higher reactivity near the surface of the member is preferable.

It is preferable that the first and the second molecules are supplied as a gas diluting the first molecule and a gas diluting the second molecule or as a mixed gas diluting the first and the second molecules to the surface of the member and microwave is applied to at least one of the gas diluting the first molecule, the gas diluting the second molecule and the mixed gas.

It is preferable that the frequency of the microwave is 3 GHz or more.

It is preferable that at least one of the gas diluting the first molecule, the gas diluting the second molecule and the mixed gas is a gas consisting of molecules having vibrational degrees of freedom of 60 or less.

It is preferable that the treating the surface of the member with the cluster includes oxidizing the surface of the member or the contamination adhered on the surface of the member.

It is preferable to comprise further treating the surface of the member using any of a gas having reactivity with an oxide or a chelating agent forming a chelate compound with metal after or together with treating the surface of the member with the cluster.

It is preferable to comprise further physically removing a residual product produced on the surface of the member by treating the surface of the member with the cluster.

It is preferable that treating the surface of the member with the cluster is at least one step selected from a group consisting of a step of cleaning the surface of the member, a step of forming a film on the surface of the member and a step of etching the surface of the member.

It is preferable that the member is a semiconductor substrate and treating the surface of the member with the cluster is at least one step selected from a group consisting of a step of cleaning the surface of the semiconductor substrate, a step of forming a silicon oxide film on the surface of the semiconductor substrate, a step of forming a metal oxide film on the surface of the semiconductor substrate, a step of forming a film by a chemical vapor phase deposition on the surface of the semiconductor substrate, a step of forming a film by a physical vapor phase deposition on the surface of the semiconductor substrate, a step of thermal treatment of the surface of the semiconductor substrate and a step of dry etching

of the surface of the semiconductor substrate.

The present invention provides a surface treating method for a substrate comprising;

producing a cluster having a first molecule and a second molecule bonded together by inter molecular forces, wherein the first molecule having a higher reactivity than that of the first molecule when it is not bonded with the second molecule which is different from the first molecule; and

treating a surface of the substrate with an atmosphere of said cluster containing at least the first molecule having the higher reactivity.

It is preferred that the first molecule made higher reactivity contains oxywater.

The present invention provides a surface cleaning method for the surface of a member, comprising;

producing a cluster having a hydrogen peroxide molecule and a water molecule bonded together by an inter molecular force in a vapor phase; and

cleaning the surface of the member in a vapor phase with the cluster.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph showing the potential energy changes along the reaction paths of the production of H_2OO from H_2O_2 in a gas phase;

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Fig. 2 shows a structural change of an isolated H_2O_2 molecule in the production of H_2OO from H_2O_2 in a gas phase;

Fig. 3 shows a structural change of an H_2O_2 molecule with an H_2O molecule in the production of H_2OO from H_2O_2 in a gas phase;

Fig. 4 shows a structural change of an H_2O_2 molecule with two H_2O molecules in the production of H_2OO from H_2O_2 in a gas phase;

Fig. 5 shows a structural change of an H_2O_2 molecule with a dimmer of H_2O molecules in the production of H_2OO from H_2O_2 in a gas phase;

Fig. 6 shows a structural change of an H_2O_2 molecule with three H_2O molecules in the production of H_2OO from H_2O_2 in a gas phase;

Fig. 7 is a graph showing the potential energy changes along the reaction paths of the production of H_2OO from H_2O_2 in a liquid phase;

Fig. 8 shows a structural change of an H_2O_2 molecule in a liquid phase in which no H_2O molecule is participated;

Fig. 9 shows a structural change of an H_2O_2 molecule in a liquid phase in which one H_2O molecule is participated;

Fig. 10 schematically shows the surface treating method according to an embodiment of the present invention;

Fig. 11 schematically shows the surface treating method according to an embodiment of the present invention; and

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Fig. 12 schematically shows the surface treating system according to an embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a surface treating method characterized that a cluster bonded by the first molecule to the second molecule by an intermolecular force is produced in a gas phase and at least a part of internal energy released in producing the cluster makes the first molecule contained in the cluster more reactive and the surface of the member is treated in a gas phase with the cluster containing the first molecule made in a state of higher reactivity.

The cluster means 2 or more molecules bonded together by an intermolecular force. It is preferable that the molecules is less than 50 at view of the effect that one molecule is influenced by the molecules around the one molecule in a typical liquid phase.

Large energy is usually necessary for making the first molecule or that contained in the cluster consisting of the first molecule only into a state of higher reactivity and, therefore, it is quite difficult to produce such a reactive chemical species in high concentrations.

In the present invention however, when the first molecule is made into a state of higher reactivity, a cluster in which the first molecule and the second molecule are bonded by means

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of an intermolecular force is produced. Such a cluster is stabilized by the amount of interaction energy of the first molecule with the second molecule. Further, in the present invention, internal energy released in producing the cluster is utilized for making the first molecule into a state of higher reactivity. Accordingly, according to the present invention, it is possible to make the first molecule higher reactivity by merely giving a very low energy to the cluster with no energy from outside in an ideal manner.

Optimum state of the second molecule exists in order to make the first molecule higher reactivity. The energy to achieve the optimum state of the second molecule may be given to the cluster from outside of the system. The energy given from outside of the system depends upon the numbers of the molecules constituting the cluster, i.e. upon the structure of the cluster. Optimum cluster structure varies depending upon the kind of the first and the second molecules but, when the liquid phase acts merely as uniform dielectrics, reaction barrier is not reduced effectively. Thus, in order to make the first molecule higher reactivity by low activation energy, it is needed to use neither liquid phase consisting of the first and the second molecules nor usual gas phase composed of just a mixture of the first and the second molecules but to use a cluster comprising the first and the second molecules bonded by an intermolecular force to utilize the internal energy released in producing the

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cluster.

In the present invention, the first molecule and the second molecule may be the same kind of molecules or different kind of molecules. It is preferred that the second molecule acts as a catalyst so that the first molecule contained in the cluster is made higher reactivity.

In the present invention, hydrogen peroxide molecule may be used as the first molecule and water molecule may be used as the second molecule for example. In that case, it is preferred that the reaction is controlled so as to form a cluster consisting of one molecule of hydrogen peroxide and three molecules of water. Endothermic energy to produce oxywater (or water oxide; H_2OO) consisting of a H_2O_2 molecule and three molecules of water from such monomers, i.e. an apparent reaction barrier, can be made nearly zero. In other words, it is possible that the total potential energy when those molecules are mutually positioned unlimitedly far (i.e., the total potential energy of dissociation limit) and the total potential energy of the cluster consisting of three molecules of water and oxywater are made nearly the same. It is important that reducing the apparent reaction barrier is not attributed from effect of local electric field due to the dielectric nature of hydrogen peroxide or water but from intermolecular interaction itself between hydrogen peroxide molecule and water molecule. Accordingly, useful oxywater for various surface treating can be efficiently

produced in a gas phase under controlled.

In order to regulate the reaction so as to produce a cluster consisting of one molecule of hydrogen peroxide and three molecules of water, it may make the molar ratio of hydrogen peroxide to water about 1:3 not at the stage of introduction of the gases into a treating vessel but on the surface of the member. In that case, it is preferable that the molar ratio hydrogen peroxide to water from 1:2.5 to 1:3.5, more preferable from 1:2.75 to 1:3.25.

In that case, it is possible that the exothermic energy for producing a cluster consisting of oxywater and three molecules of water from those monomers is made nearly zero.

Incidentally, under the situation where the intermolecular collision is vigorous, lifetime of oxywater is not so long. Therefore, it is preferred that producing oxywater is carried out near the member. Further, the apparent reduction in the reaction barrier for producing oxywater is measured from a dissociation limit. Therefore, when energy released in producing a cluster of hydrogen peroxide with water cannot be utilized for producing oxywater or, in other words, when the energy is lost by excitation of vibrational or rotational states due to collision of clusters, then it is difficult to reduce apparent reaction barrier. Accordingly, it is important to suppress the collisional relaxation and also to produce an oxidizing species near the surface of the member.

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In order to prevent the undesired collisional relaxation, reaction of hydrogen peroxide with water should not be carried out in a bulk of liquid phase and vapor phase but they may be separately supplied to the surface of the member. In that case, producing the oxidizing species near the surface of the member can be also done easily.

Also, in the case of using additional gases, it is same as above described. It is important to use the additional gases as small vibrational degrees of freedom as possible. It is preferred that the additional gases have vibrational degrees of freedom of 60 or less.

They may be also supplied to the surface of the member as a mixed gas of hydrogen peroxide with water. For example, it is possible that a cluster of hydrogen peroxide and water is prepared in a bulk of gas phase having a smaller density of three or more order of magnitude as compared with liquid phase and the resulting cluster is supplied to the surface of the member together with suppressing the collisional relaxation. Incidentally, when hydrogen peroxide and water are supplied as a mixed gas to the surface of the member, it is preferred that the total gas pressure is 1 atmospheric pressure or lower.

In order to suppress undesired clustering of hydrogen peroxide and/or water and also to prepare a cluster of them a desired size, irradiation of microwave is effective. When microwave is irradiated to hydrogen peroxide and water, their

molecules are subjected to a rotational excitation and, therefore, cluster of a desired size (cluster composed of desired numbers of molecules) can be selectively prepared.

For example, when microwave of frequency of 3.4 GHz or more is irradiated, H_2O cluster that consists of three or less molecules can be selectively supplied. When microwave of frequency of 3.2 GHz or more is irradiated, H_2O_2 cluster that consists of two or less molecules can be selectively supplied. Accordingly, irradiation of microwave of frequency of 3 GHz or more is preferred, irradiation of microwave of frequency of 3.2 GHz or more is more preferred and irradiation of microwave of frequency of 3.4 GHz is still more preferred.

The above-mentioned method of the present invention can be applied to various surface treating using an oxidizing species. For example, in a fabrication process of semiconductor devices, it can be utilized for a cleaning treatment of a semiconductor substrate. It can be also utilized for the formation of various oxide films such as silicon oxide film and metal oxide film, for the heating treatment after their formation and for a dry process requiring an oxidizing species such as a dry etching process. The method of the present invention may also be applied not only to a process for the fabrication of semiconductor devices but also to a process for the manufacture of other substances.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

As hereunder, the present invention will be illustrated in more detail. Incidentally, the following illustration will be made for the case where hydrogen peroxide molecule and water molecule are used as the first and the second molecules, respectively, although that will also be similar for the cases where other chemical substances are used.

As the temperature rises, pure water becomes acidic and, at the same time, reduces its electric resistibility and viscosity coefficient. That is caused by an increase in degree of dissociation and by changes in the cluster structure of water. Changes in physical property of pure water as such are also resulted by such excitation methods other than temperature rise as electrolysis and application of microwave, magnetic field and ultrasonic wave, although their mechanism has not been so well clarified yet. As hereunder, the result of theoretical investigation by means of quantum chemistry on efficient production method of oxidizing species (including by means of irradiation of microwave) in a system containing pure water and hydrogen peroxide will be mentioned.

First, it was tested whether H_2O cluster and H_2O_2 cluster consisting of desired number of molecules can be selectively supplied by irradiation of microwave. Thus, rotational constants of H_2O cluster and H_2O_2 cluster were calculated and the resonance condition for selecting the cluster of the desired

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size by microwave excitation was clarified. The results are
shown in the following Table 1 and Table 2, respectively.

n	structure	Bx	By	Bz
1	-a)	796.05	433.51	280.67
2	linear a)	214.32	6.388	6.387
3	cyclic a)	6.842	6.770	3.466
4	cyclic a)	3.587	3.587	1.824
5	cyclic a)	2.030	2.019	1.033
6	cage b)	2.241	1.151	1.103
6	prism b)	1.697	1.417	1.358
6	cyclic b)	1.241	1.241	0.632
8	box b)	0.909	0.909	0.853

Table. 1 : Rotational constants of $(H_2O)_n$ clusters

at the MP2/aug-cc-pVDZ level of theory. [GHz]

a) Geometry were optimized by analytic derivative method

b) Geometry were optimized by numerical derivative method

n	structure	Bx	By	Bz
1	-a)	296.37	25.88	25.06
2	linear a)	13.56	3.263	3.225

Table. 2 : Rotational constants of $(H_2O_2)_n$ clusters

at the MP2/aug-cc-pVDZ level of theory. [GHz]

a) Geometry were optimized by analytic derivative method

Incidentally, it is easily presumed that the more the
cluster size, the more the rotational moment whereby the less

the rotational constant. Accordingly, with regard to an H_2O cluster, calculation was carried out up to the cluster consisting of 8 molecules.

The H_2O cluster can take various stable (local minimum) structures and, as will be clear from the Table 1, the rotational constant tends to increase as the size of the cluster decreases. For example, it is noted that, in order to select a cluster consisting of 4 or less molecules, microwave of about 3.4 GHz or more is to be irradiated. As to an H_2O_2 cluster, calculation was carried out up to the cluster consisting of 2 molecules only as shown in the Table 2 but, since the monomer *per se* has an O-O bond whereby its rotational moment is larger than H_2O, it is noted that its rotational constant is very small as compared with an H_2O cluster. For example, in selecting the cluster consisting of two or less molecules, it is noted that microwave of about 3.2 GHz or more is to be irradiated.

Then various decomposition processes of hydrogen peroxide were investigated. Incidentally, at this time, the changes in energy and structure of isolated cluster consisting of one molecule of H_2O_2 and 0-3 molecule(s) of H_2O *in vacuo* was investigated along various reaction paths without taking the "solvent effect" by water in the bulk of liquid phase into consideration. Specific method for the calculation is as follows. The solvent effect is considered later.

Changes in energy (potential energy surface or PES) along

the various reaction paths of the chemical reactions represented by

$$H_2O_2 + nH_2O \rightarrow H_2OO \cdot nH_2O \text{ (n: an integer of 0-3)}$$

$$H_2O_2 \rightarrow 2OH$$
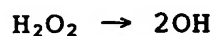
were calculated by a density functional method (BHandHLYP) and a second-order Møller-Plesset perturbation method (MP2) with a Hartree-Fock configuration as a reference space. The basis set employed is the augmented correlated set aug-cc-pVDZ which is optimized for a post Hartree-Fock calculation.

Incidentally, energy value given hereinafter is the value at the MP2/aug-cc-pVDZ level of theory unless otherwise mentioned. The energy value given hereinafter is that obtained by comparing the internal energy ("electronic" energy or E_{elec}) only and does not include solvation energy (E_{solv}), kinetic energy, zero point vibrational energy (ZPE), vibrational/rotational/translational energies ($E_{vib}/E_{rot}/E_{trans}$) and entropy term (S) ($E_0 = E_{elec} + ZPE$; $E = E_0 + E_{vib} + E_{rot} + E_{trans}$; $H = E + RT$; $G = H - TS$; R is gas constant; T is absolute temperature).

Result of calculation concerning the system in which one molecule of H_2O is participated in the formation of oxywater from H_2O_2 was identical with that mentioned in the literatures such as *J. Am. Chem. Soc.*, vol. 113, (1991) 6001, etc. With regard to the system in which two molecules of H_2O are participated, the result was also same as that mentioned in the above literature

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when each of the two H_2O molecules independently interacts with H_2O_2. However, when the fact that H_2O is apt to form an oligomer by a hydrogen bond is taken into consideration, it is necessary to consider the hydrogen transfer of both intramolecular (within an H_2O_2 molecule) and intermolecular (between an H_2O_2 and an H_2O) paths when an H_2O dimer comes close to the H_2O_2 molecule. As to the system where three H_2O molecules are participated in, it is also necessary that the formation of an H_2O oligomer is taken into consideration. Since those are not disclosed in the above literature, consideration therein will be carried out here.

First, PES in which 1-3 molecule(s) of H_2O is/are participated will be briefly mentioned. When one H_2O molecule is participated in, it has been found that a reaction barrier of oxywater formation is lower to an extent of not less than 10 kcal/mol via an intermolecular hydrogen transfer (concerted 1,4-hydrogen shift) path than via an intramolecular hydrogen transfer (1,2-hydrogen shift) path. The former process does not take place in the case of one isolated H_2O_2 molecule and shows a catalytic effect of an H_2O molecule. When two molecules of H_2O are participated in, it has been also found that, as compared with the intramolecular hydrogen transfer path, the barrier is lower to an extent of not less than 10 kcal/mol in the intermolecular hydrogen transfer path.

It is particularly noteworthy that, when two molecules

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of H_2O are participated in, although the reaction barrier in the reaction to produce H_2OO from H_2O-adsorbed H_2O_2 lowers to an extent of only about 4 kcal/mol as compared with the case of participation of 1 molecule of H_2O in both intramolecular and intermolecular hydrogen transfer paths, endothermic energy for forming H_2OO measured from the dissociation limit of an H_2O_2 and two H_2Os is remarkably decreased. Therefore, the analogous investigation was carried out for the case where three molecules of H_2O were participated in whereby the same tendency was obtained and it has been noted that endothermic energy measured from the dissociation limit becomes nearly zero.

Results obtained by the above calculations are shown by a graph and figures.

Fig. 1 is a graph showing the potential energy changes along the reaction paths of producing H_2OO from H_2O_2 in a gas phase. Incidentally, changes in the structure along the reaction paths shown in Fig. 1 are shown in Fig. 2 to Fig. 6. The Table 3 summarizes the results for clarifying the relation between the energy changes and the number of H_2O. Table3

levels of theory	H_2O adsorption	activation energy 1,2 H-shift (intra) $(E_{a;1,2Ts}^{for})$	stabilization energy after 1,2TS $(E_{a;1,2TS}^{rev})$	activation energy 1,4 H-shift (inter) $(E_{a;1,4TS}^{rev})$	stabilization energy after 1,4TS $(E_{a;1,4TS}^{rev})$
n=0	-	57.144	7.454	-	-
n=1	7.626	49.291	11.744	37.863	0.317
n=2 2-mono.	16.018	48.559	19.385	31.512	2.338
n=2 1-di.	18.205	45.319	13.041	33.133	0.856
n=2 1-di.	18.589	45.578	12.778	33.639	0.838
n=2 1-di.	18.589	46.389	12.859	34.686	1.158
n=3 di.& mono.	27.163	46.156	21.101	27.637 (d) 28.391 (m)	2.582 (d) 3.336 (m)
n=3 di.& mono.	27.567	45.943	20.761	27.858 (d) 28.507 (m)	2.676 (d) 3.325 (m)
n=3 di.& mono.	26.709	46.100	20.902	28.268 (d) 28.509 (m)	3.070 (d) 3.310 (m)

Table. 3 : Reaction energies of H_2O_2 + nH_2O → $H_2OO \cdot nH_2O$ (n=0~3) systems at the MP2/aug-cc-pVDZ level of theory [kcal/mol]

Fig. 1 shows potential energy surfaces obtained at the MP2/aug-cc-pVDZ level of theory for the case where 0-3 molecule(s) of H_2O is/are participated in a reaction of forming H_2OO from one molecule of H_2O_2 in a gas phase. When H_2O is not participated in as shown in Fig. 2 (in Fig. 1, it is shown as isolated H_2O_2), H_2OO is formed via a transition state that one of the H atoms in the H_2O_2 molecule produces moves between two O atoms. This transition state is a so-called late transition state near H_2OO and the reaction barrier is surprisingly high (57.14 kcal/mol). By calculating the potential energy surface

of the dissociation of O atom from H_2OO, it has been found that irradiation of electromagnetic field of 0.4 eV or more energy will promote the dissociation if the condition for intersystem-crossing of singlet-triplet is achieved while, for the usual spin-conserved dissociation, irradiation of electromagnetic field of 1 eV or more energy will do.

When one molecule of H_2O is participated in (shown as $1H_2O$ at n=1 in Fig. 1), the H_2O molecule is adsorbed as shown in Fig. 3 by a bifunctional (both proton-donative and proton-acceptive character) formation of two hydrogen bonds with H and O atoms of an H_2O_2 molecule. In a path of intramolecular hydrogen transfer within an H_2O_2 molecule, $H_2OO.H_2O$ is formed via a transition state of a 1,2-hydrogen shift that is substantially equivalent to the case where no H_2O molecule is participated in. As shown in Fig. 1, the barrier in this case (49.29 kcal/mol) decreases by 8 kcal/mol as compared with the barrier when no H_2O molecule is participated in. On the other hand, along a path of intermolecular hydrogen transfer between H_2O_2 and H_2O molecules, $H_2OO.H_2O$ is formed via a transition state of a 1,4-hydrogen shift. The barrier in that case (37.87 kcal/mol) is lower by 10 kcal/mol as compared with that of 1,2-hydrogen shift.

When two molecules of H_2O are participated in, there will be four reaction paths, i.e. three paths where two molecules of H_2O form a dimer followed by adsorbing with an H_2O_2 molecule

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and another path where each of two H_2O molecules is adsorbed with an H_2O_2 molecule as a monomer. As shown in Fig. 4, when each of two H_2O molecules is adsorbed with an H_2O_2 molecule as a monomer (shown as $2H_2Os$ in Fig. 1), barrier of 1,2-hydrogen shift which is an intramolecular hydrogen transfer path is 48.56 kcal/mol while that of 1,4-hydrogen shift which is an intermolecular hydrogen transfer path is 31.51 kcal/mol. The former is nearly the same as in the case where one molecule of H_2O is participated in but, in the latter, there is a decrease of 6 kcal/mol as compared with the case of one H_2O participant.

On the other hand, with regard to the three paths where two molecules of H_2O form a dimer and adsorb with an H_2O_2 molecule as shown in Fig. 5 for example, H in one H_2O forms hydrogen bond as proton donors with O in an H_2O_2, and simultaneously O in the other H_2O forms hydrogen bond as proton acceptor with H in an H_2O_2. The barriers (in the order of intramolecular and intermolecular hydrogen transfers) were path 1 (45.32, 33.13), path 2 (45.58, 33.64) and path 3 (46.39 and 34.69) kcal/mol, respectively.

It is noted from the above that, when two molecules of H_2O form a dimmer and adsorb with H_2O_2, the adsorption state is stabilized to an extent of a hydrogen bond between two H_2O molecules as compared with the case of adsorption as a monomer and that, due to more stabilization of 1,2-hydrogen shift transition state than that, barriers of the intramolecular

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hydrogen transfer paths decrease to an extent of about 4 kcal/mol. Such a decrease is due to the fact that an interaction between an H atom of H_2O molecule positively polarized by formation of a dimer and an O atom of H_2O_2 molecule negatively polarized by an intramolecular hydrogen transfer process is enhanced or, in other words, energy required for relaxation of internal strain of H_2O_2 molecule by an H_2O molecule which is a catalyst (which is shown in the LUMO, HOMO and 2nd HOMO shift).

On the other hand, in a system in which two molecules of H_2O are participated, barriers in intermolecular 1,4-hydrogen shift paths where H_2O is adsorbed as a dimer increase to an extent of about 2 kcal/mol as compared with the case where H_2O is adsorbed as two monomers. This is because, in the 1,4-hydrogen shift transition state, dimer paths are only a little more stable than a monomer path but H_2O-adsorbed states are more stable than that in dimer paths. Incidentally, it is same in the 1,4-hydrogen shift transition state as well that, there is a strong interaction between an H atom of a positively polarized H_2O molecule by formation of a dimer, and an O atom of a negatively polarized H_2O_2 molecule by an intermolecular hydrogen shift.

A particularly noteworthy point for both the system in which one H_2O molecule is participated and the system in which two H_2O molecules are participated is that, in the system where two H_2O molecules are participated in, endothermic energy upon

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production of oxywater measured from a dissociation limit is significantly decreased as compared with the system where one H_2O molecule is participated in regardless of monomer and dimer paths. Such a tendency is more significant particularly in an intermolecular hydrogen transfer path. The above result shows that, in a process where the absorption energy resulted upon adsorption of H_2O molecule with H_2O_2 molecule is not dispersed (or relaxed) but is conserved as an excess internal energy, or in a gas phase processes (dry processes), the adsorption energy can be effectively utilized to the above endothermic energy (external work).

When three molecules of H_2O are participated in, several reaction paths may be considered as well. When the third H_2O molecule is added to a system in which two molecules of H_2O are participated in as a dimer, it is easily presumed that the interaction is the strongest in the case where the third H_2O molecule is adsorbed by formation of a hydrogen bond in a bifunctional manner with a H_2O_2 molecule. When the first and the second H_2O molecules interact with an H_2O_2 molecule by dimer paths, the third H_2O molecule is able to independently form hydrogen bonds with an H_2O_2 molecule in a bifunctional manner. Thus, as shown in Fig. 6, the case where a dimer comprising the first and the second H_2O molecules interacts with one HOO structure of the H_2O_2 molecule while the third H_2O molecule interacts with another HOO structure may be considered.

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On the other hand, when the first and the second H_2O molecules interact with an H_2O_2 molecule via a monomer path, proton-donating site of the H_2O_2 molecule is exhausted and, therefore, it is disadvantageous that the third H_2O molecule independently interacts with an H_2O_2 molecule. Accordingly, there is no way but the third H_2O molecule interacts with the first or the second H_2O molecules. Thus, any of the first and the second H_2O molecules forms a dimer structure with the third H_2O molecule whereupon the final adsorption structure becomes identical with the dimer paths just-above mentioned.

Characteristics in the case wherein three H_2O molecules are participated will be summarized as follows.

(1) Adsorption energy as a result of adsorption of the third H_2O molecule increases to an extent of 8-10 kcal/mol more as compared with the system in which two H_2O molecules are participated.

(2) Once after adsorption of an H_2O dimer, the difference between the barrier of intermolecular hydrogen transfer between H_2O_2 and H_2O monomer and the barrier of intermolecular hydrogen transfer between H_2O_2 and H_2O dimer is as little as 1 kcal/mol or less.

(3) A 1,4-hydrogen shift barrier from an adsorption state is about 28 kcal/mol while a 1,4-hydrogen shift barrier measured from a dissociation limit is nearly zero.

Thus, when a reaction condition is controlled so as to

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form a cluster consisting of one H_2O_2 molecule and three H_2O molecules, oxywater that is an oxidizing species can be efficiently produced.

Now, in order to show that the result obtained by the above investigation is characteristic in a gas phase reaction and is advantageous in terms of reaction potential energy as compared with the reaction under a simple wet (liquid pahse) condition, reaction paths in uniform dielectrics (water having a specific dielectric constant $\varepsilon = 78.3$) was investigated by an SCRF method (Self-Consistent Reaction Field method) for a reaction system wherein no and one H_2O molecule is participated. First, calculation method therefor will be explained as follows.

In water of a standard state, about 10-50 water molecules take a cooperative motion due to a hydrogen bond between them and a dipole interaction whereupon an environment showing a specific dielectric constant of $\varepsilon = 78.3$ is formed. This environment can be of course reproduced if a huge cluster model is used. A solvent effect model is also efficient, where environmental water of surroundings around the chemically active center (reaction site) is homogeneously incorporated as a macroscopic medium having a specific dielectric constant ε and the said means is applicable to an organic solvent environment as well. Here, a system of $H_2O_2 + nH_2O$ (n = 0, 1) was used and the change in a reaction potential surfaces with and without the consideration of the solvent effect was

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investigated.

Consideration of the solvent effect was carried out using two kinds of reaction field models of solvation where a method of locating a solvate molecule into cavities in uniform dielectrics is different each other. Incidentally, one of the models is the simplest model and is known as the Onsager model (dipole and sphere model) where a molecule having an electric dipole moment is placed into a predetermined fixed spherical cavity having a desired size. Here, a region where radius a_{0-} of the spherical cavity is a value where 0.5 Å which is a typical van der Waals radius of a solvent molecule is added to the radius of a region giving the electron density of 0.001 electrons/bohr^3 by a Monte-Carlo calculation.

Another model is an SCIPCM (Self-Consistent Isodensity Polarized Continuum Model) where isodensity surface (0.004 au) of a solute molecule is adopted as a cavity and the cavity shape is determined self-consistently with regard to the charge density in order to minimize the total energy including solvation energy.

BHandHLYP/aug-cc-pVDZ level of theory was employed. And the results will be explained below by referring to Fig. 7.

Fig. 7 is a graph showing potential energy changes along the reaction paths of the production of H_2OO from H_2O_2 in a liquid phase. Changes in energy are summarized in Table 4 and Table 5. Incidentally, structural change along the each reaction

shown in Fig. 7 is shown in Fig. 8 and Fig. 9 in which Fig.
8 shows a structural change in the reaction wherein no H_2O molecule
is participated while Fig. 9 shows a structural change in the
reaction wherein one H_2O molecule is participated. Round line
given around the each structure of "solute" cluster in Fig.
8 and Fig. 9 show spherical cavity of radius a_0 mentioned above
in the case of an Onsager model while, in the case of an SCIPCM
model, they show isodensity surfaces of 0.0004 au, respectively.

Levels of theory	activation energy (E_a^{for})	stabilization energy after TS (E_a^{rev})
gas $\varepsilon=1$(MP2)	57.144	7.454
gas $\varepsilon=1$	56.179	12.037
Onsager $\varepsilon=78.3$	55.019	17.692
SCIPCM $\varepsilon=78.3$	54.264	19.805

<u>Table. 4</u> : Reaction energies of $H_2O_2 + nH_2O \rightarrow H_2OO \cdot nH_2O$ (n=0) system

in both gas and liquid phases.

at the BHandHLYP/aug-cc-pVDZ level of theory [kcal/mol]

levels of theory	H$_2$O adsorption	activation energy 1,2 H-shift (intra) (E$_{a;1,2TS}^{for}$)	stabilization energy after 1,2TS (E$_{a;1,2TS}^{rev}$)	activation energy 1,4 H-shift (inter) (E$_{a;1,4TS}^{rev}$)	stabilization energy after 1,4TS (E$_{a;1,4TS}^{rev}$)
gas ε=1 (MP2)	7.626	49.291	11.744	37.863	0.317
gas ε=1	7.031	51.585	17.276	38.714	4.405
Onsager ε=78.3	8.939	51.933	15.130	41.658	4.855
SCIPCM ε=78.3	5.217	51.952	20.326	37.697	6.071

Table. 5 : Reaction energies of H$_2$O$_2$ + nH$_2$O → H$_2$OO·nH$_2$O (n=1) system

in both gas and liquid phases.

at the BHandHLYP/aug-cc-pVDZ level of theory [kcal/mol]

It has been noted from the change in geometry that the more the polarization in the structure (transition state, producing system), the more the change although it is less than about 2% between the cases of the presence and the absence of a reaction field (dipolar field).

First, an autolytic reaction of H$_2$O$_2$ wherein H$_2$O is not participated will be considered. An autolytic reaction of H$_2$O$_2$ in a gas phase (ε = 1) is an endothermic reaction having a very high barrier in both of a path forming two OH radicals and a path producing H$_2$OO (→ O atom) and photodissociation and metal catalyst are needed to promote the reaction. Such a tendency was unchanged even when the reaction field was taken into

consideration. Reduction in a reaction barrier is only about 1 kcal/mol in an Onsager field and is about 2 kcal/mol in an SCIPCM field. Absolute value of Mulliken charges on each atom increases in the order of gas phase → Onsager field → SCICPM field. Accordingly, electric dipole moment as a molecule increases as well although the amount of the change from the initial state to the transition state is almost equal.

Therefore, the difference in the reaction field corresponding to the difference in induced electric dipole moment becomes small. Finally, although the PES from the initial state to the transition state is nearly same, the PES from the transition state to the product (H_2OO) is considerably different and the stabilization energy (or, in other words, barrier of reverse reaction) increases by about 5-8 kcal/mol. Changes in Mulliken charge in gas phase and liquid phase (SCRF models) are also very large as compared with those of the initial state and the transition state. H_2OO itself is greatly polarized and, therefore, an O atom having an excess negative charge expresses a strong oxidative property and reaction field further promotes such a large polarization.

It is preferred for an autolysis that stabilization of H_2OO (product) is increased by a solvent effect. However a decrease in a reaction barrier to the forward direction exceeding 50 kcal/mol is small and, accordingly, a solvent effect to autolysis by an H_2O_2 molecule alone cannot be expected.

Therefore, the solvent effect in the case of participation of H_2O (one molecule) where a catalytic effect has been confirmed in a "gas phase" reaction system will be considered.

First, in an adsorption structure of H_2O with H_2O_2, a structure where H_2O interacts with H_2O_2 in a bifunctional, i.e. proton donative/acceptive, manner is obtained in a gas phase while, under a uniform dielectric environment, H_2O takes a structure of being adsorbed with H_2O_2 as a proton acceptor.

In a transition state, H_2O where electric dipole moment is larger by about 20% is more than H_2O_2 strongly affected by a reaction field of "water having $\varepsilon = 78.3$". Accordingly, hydrogen bond formation between O atom of H_2O_2 and H atom of H_2O is suppressed in the case of an intramolecular hydrogen shift process. That weakens the effect of promotion of negative polarization of O atom that is to express the oxidative property. Even in the case of an intermolecular hydrogen shift process, O atom in H_2O effectively works for abstracting of H from H_2O_2 as a proton acceptor during the step from adsorption to transition state but an effect of promotion of O and H donation to H_2O_2 is small.

Therefore, changes in the reaction barrier due to reaction field are very small in both intramolecular and intermolecular hydrogen shifts. Rather, a decrease in barrier by a participation of H_2O molecule (4–5 kcal/mol) is larger and far more effective than that ; the difference of 5 kcal/mol at around

room temperature corresponds to a difference of 500-times in the speed estimated by Boltzmann factor.

The above suggests that the barrier decrease in a reaction system of H_2O_2 molecule with plural H_2O molecules is not characteristic in a liquid phase due to an dielectric interaction but is rather achieved only by a cooperative reaction with H_2O_2 and H_2O as already clarified in a gas phase reaction system.

Finally, since polarization of the product H_2OO that is an oxidative species becomes largest on a PES, a large effect of the reaction field is expected. The result of an SCIPCM field that is more appropriate reaction field model supports that, in both intramolecular and intermolecular hydrogen shifts, stabilization energy becomes larger although the degree is small.

On the contrary, that is not always the case in an Onsager field 'model. Although the polarization at the H_2OO side increases due to the reaction field, that at the H_2O side is rather smaller than in a gas phase system. The most noteworthy thing concerning the oxidative property of H_2OO is that, although the size of negative charge of O atom that is to express an oxidative property becomes large by taking the reaction field into consideration, it does not additional change even when one molecule of H_2O is participated therein.

In the case of a gas phase reaction system, when the number of catalytic H_2O molecule increase as 0, 1, 2 and 3, the Mulliken

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charge of this O atom that is express an oxidative property

increases -0.5052 (no H_2O molecule), -0.5394 (one H_2O molecule),

from -0.5662 to -0.5902 (two H_2O molecules) and from -0.5981

to -0.6180 (three H_2O molecules) (values at the MP2/aug-cc-pVDZ

level of theory). In an SCRF model used at this time, although

the charge distribution has not achieved the experimental value

yet, the effect of the reaction field may be almost saturated

when $\varepsilon = 78.3$. Thus, even when many H_2O molecules try to promote

the polarization of H_2OO as a liquid phase (for example, as

an average sum of electric dipoles in various directions), it

is likely that the resulting effect is almost saturated in the

polarized value obtained by these calculations.

However, when plural H_2O molecules interact "in an optimum

steric configuration" as in a gas phase reaction system,

polarization of H_2OO is still promoted by at least up to 3

molecules of ancillary H_2O. Reactivity (oxidative property)

of H_2OO can be controlled whether the electric dipole interaction

from plural H_2O molecules is utilized "homogeneously" or

"orientation-dependently". That is the second advantage by

the use of a gas phase reaction system instead of a liquid phase

one based upon a dielectric interaction. The first advantage

is, of course, a decrease in the reaction barrier.

To sum up, it has now been clarified from the consideration

of the reaction field that:

(1) in both of an H_2O_2 autolytic reaction system and a

one-molecular H_2O catalytic system, a decrease in a reaction barrier noted is as small as 1-2 kcal/mol at best; and

(2) although the Mulliken charge (polarization charge) on each atom which is an index for an oxidative property of an oxidative species (H_2OO) becomes large when the reaction field is taken into consideration, there is no additional change even if H_2O is participated therein.

From the above, it has been clarified that the catalytic effect of H_2O, i.e. an enhancing effect of oxidative property and an apparent reaction barrier decrease

(3) is not due to an dielectric character which is caused by H_2O as a group and

(4) is an intermolecular direct reaction characteristic in a gas phase reaction system which is only achieved by a cooperative reaction of H_2OO with H_2O.

The above suggests that, in promotion of formation of an oxidative species in an $H_2OO + nH_2O$ system and in control their oxidative property, water molecule in such numbers that causes a dielectric property (e.g., liquid or solid phase) is not necessary whereby that is able to contribute in the reduction of the using amount of pure water.

However, in order to effectively utilize the apparent barrier decrease, it is important as a process condition that the adsorption energy of H_2O with a H_2O_2 molecule should not be dispersed but is conserved as an internal energy or that

collisional relaxation of the reaction product should be suppressed although such a control in a liquid phase is difficult. Accordingly, the conclusion is that the production of oxywater is effective in carrying out in a gas phase reaction system. Instead of that, with regard to the removal of contamination, it is necessary to consider in a step corresponding to removal of metal ion by hydration that is an advantage of the liquid phase reaction system and to static electrical removal of particles by means of a zeta-potential regulation.

Result of the theoretical investigation concerning the intramolecular and the intermolecular hydrogen transfer process by one molecule of H_2O_2 and up to three molecules of H_2O as mentioned above will be summarized as follows.

When the gas phase reaction system is achieved, an effect of reducing the barrier by oligomerization of H_2O molecule as a catalyst is noted in an intramolecular hydrogen transfer process in H_2O_2. With regard to an intermolecular hydrogen transfer process between H_2O_2 and H_2O, an effect by oligomerization of H_2O molecule is not noted although a barrier decrease is resulted. Especially, the endothermic energy measured from the dissociation limit, i.e. the apparent reaction barrier, significantly decreases and, when three molecules of H_2O are participated therein, it can be made almost zero. On the other hand, when the conventional liquid phase reaction is considered merely as an effect of local electric field by

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dielectric property of hydrogen peroxide or water, the above apparent reaction barrier rather increases.

From those results, in order to produce an oxidative species in high efficiency in the system of hydrogen peroxide and water, it is preferred to satisfy the following requirements. Thus, one molecule of hydrogen peroxide is suppressed with three molecules of water. In addition, hydrogen peroxide is not made to react with water in a bulk of a liquid phase or a gas phase but each of them is separately supplied near the surface of the member followed by making to react them. Alternatively, when their cluster is formed in a bulk of gas phase where the density is smaller to an extent of 3 or more order of magnitude as compared with a liquid phase, the cluster having the excess internal energy conserved during the cluster formation is supplied onto the surface of the member together with suppressing the loss of the energy by collisional relaxation whereupon an oxidative species is produced just on the surface of the member. Still alternatively, in order to supply hydrogen peroxide and water on the surface of the member together with suppressing their clustering, microwave of 3 GHz or more where rotational excitation of H_2O trimer, H_2O dimer, H_2O monomer, H_2O_2 dimer and H_2O_2 monomer are possible is applied. As a result of adoption of at least one of them, it is possible to produce an oxidative species in higher efficiency.

Now, the surface treating using the oxidative species

produced by the above-mentioned method will be explained.

Fig. 10 and Fig. 11 schematically show a surface treating method according to one embodiment of the present invention. In this embodiment, the case where the method of the present invention is applied to a cleaning treatment will be explained.

First, as shown in Fig. 10, microwave is irradiated to H_2O_2 and H_2O of a liquid phase or a condensed phase (such as vapor) which is essentially similar to a liquid phase. Although each of H_2O_2 and H_2O forms a cluster in a large size, it is possible to selectively prepare a cluster in a small size by irradiation of a predetermined microwave of appropriate frequency.

Then, as shown in Fig. 11, those clusters are supplied so that the molar ratio of H_2O_2 and H_2O on the surface of a Si substrate (11), which is the member to be treated on its surface, is made 1:3 for example. The clusters supplied onto the surface of the substrate (11) produce an oxidizing species such as oxywater very efficiently whereupon the organic substance (35) on the surface of the Si substrate (11) is decomposed. Metal contaminations (36) also form a metal oxide from their surface. As a result, metal contaminations (36), particles (37), etc. adhered on the surface of the substrate (11) together with the organic substance are removed. Incidentally, together with or after the decomposition of the organic substances, a fluorine-containing gas such as HF or a chelating agent forming a chelate with metal may be supplied if necessary. As a result,

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removing metal contaminations, etc. is more efficient.

As hereinabove, the case where the method of the present invention is applied to a cleaning treatment was explained and, besides the cleaning of the surface of the member, the method of the present invention is also applicable, for example, to a film-formation such as formation of a silicon oxide film and a metal oxide film, to a film-formation by chemical vapor phase growth and by physical vapor phase growth on the surface of the member and to a surface treating such as etching including a dry etching on the surface of the member.

Now, an apparatus for carrying out the above-mentioned surface treating will be explained.

Fig. 12 schematically shows a surface treating system according to an embodiment of the present invention. The surface treating system as shown in Fig. 12 is a surface treating system for the treatment of semiconductors and is mainly composed of a semiconductor treating apparatus (1) and a receiving container (2) connected thereto.

The semiconductor treating apparatus (1) is mainly composed of a treating chamber (3) and a load lock chamber (4). The treating chamber (3) and the load lock chamber (4) are connected via a gate valve (5). The load lock chamber (4) and the receiving container (2) are able to be connected by a cluster tool structure consisting of a gate valve (6) placed between them, a joint (7) connected to this gate valve (6) and a door

(8) placed at the side wall of the receiving container (2).

Incidentally, the surface treating system as shown in Fig. 12

may be in such a structure that plural treating chambers (3)

are be connected by joining to a load lock chamber (4) via a

gate valve (5).

A semiconductor treating apparatus (1) is an apparatus

that carries out at least one of dry cleaning treatment,

oxidation treatment, diffusion treatment, thermal annealing

treatment, film-forming treatment and etching treatment to the

substrate (11). An air-tight treating container (9) is

installed in a treating chamber (3) and, in this container (9),

there is provided a stand (10) on which a substrate (11) which

is the member is placed. The stand (10) is equipped with a

heating function and a cooling function whereby the substrate

temperature can be controlled. The treating container (9) is

made of a metal material such as aluminum alloy, e.g. an Al-Mg

alloy. Inner wall of the treating container (9) is usually

polished and then an oxidized passivated layer or a fluorinated

passivated layer is formed thereon or coated with other materials

such as SiO_2, SiC or SiN so that its corrosion, contaminating

the substrate (11) due to exhaust of gas or separation of heavy

metal from the wall or degradation of semiconductor devices

caused thereby are prevented.

In a treating chamber (3), there is provided a shower

head (12) opposite to the face of the stand (10) whereby plural

gases are mixed and supplied. This shower head (12) is connected to a gas supplying means (13) for supplying plural process gases to be used for the surface treating of the substrate (11) via a pipe having an opening/shutting valve (14). Incidentally, the plural gases used here mean gases comprising hydrogen peroxide and water.

In Fig. 12, only one shower head (12) and one gas-supplying means (13) are illustrated although, usually, these are installed in plural. In that case, different type of process gas is supplied from each of the gas-supplying means (13) to a shower head (12) in a desired flow rate. For example, it is possible to control the flow rate so as to make the molar ratio of hydrogen peroxide to water near the surface of the substrate (11) 1:3. Each of hydrogen peroxide and water may be supplied separately or a mixed gas thereof. Further, those gases may be diluted with other gas. Examples of such other gas are those having 60 or less vibrational degree of freedom such as rare gas, nitrogen and oxygen.

At the bottom of the treating container (9), there is provided an exhaust opening (15). The treating container (9) is connected to an exhaust (16) such as a combination of rotary pump and turbo molecular pump via the exhaust opening (15). The exhaust (16) exhausts the gas containing hydrogen peroxide, the gas containing water or the gas containing hydrogen peroxide and water in the treating container (9) to a predetermined degree

of partial pressures such as from 1013 hPa to 1×10^{-8} hPa.

Incidentally, when treatment of plasma assist such as dry cleaning treatment, etching treatment, film-formation treatment, oxidation treatment or thermal annealing treatment is carried out in a treating chamber (3), the treating container (9) is constituted in such a manner that it is electrically grounded, the stand (10) is used as a lower electrode where a high frequency electric field of 100 kHz–500 kHz, for example, is applied via a matching circuit and a shower head (12) is used as an upper electrode where a high frequency electric field of 15 GHz with a generating output of 0.3–3 kW is applied via a matching circuit.

It is preferred that the frequency of this microwave is 3 GHz or more when the fact that the frequency necessary for making water cluster consisting of three or less molecules is 3.4 GHz or more and the frequency necessary for making hydrogen peroxide cluster consisting of two or less molecules is 3.2 GHz or more is taken into consideration.

Further, in order to supply a gas containing hydrogen peroxide and water, gas supplied from a line wherefrom the vapor from an azeotropic mixture of hydrogen peroxide and water is supplied with a diluted carrier gas and another gas from a line wherefrom only steam is supplied may be used whereby the molar ratio of hydrogen peroxide to water at the position of the semiconductor substrate (11) is adjusted to 1:3.

The treating chamber (3) constituted as such and the connecting load lock chamber (4) are provided in a connectable manner by a gate valve (5), which automatically opens when a substrate (11) is carried in.

The load lock chamber (4) is in an air-tight structure and, in its inside, there is provided a conveyer (17) which conveys the substrate (11) and places the substrate (11) onto the stand (10) on the adjacent treating chamber (3). The conveyer (17) is sealed to the bottom of the load lock chamber (4) by a magnetic rail and is connected to a driver (18) located outside by means of a driving axis which is capable of rotating, moving up and down and X- and Y-axis-driving. The conveyer (17) is constituted to move forward, backward, rotatively and up-and-down by means of driving force of this driver (18).

The constitution is done in such a manner that inert gas such as nitrogen and argon or clean air is supplied into a load lock chamber (4) from a gas supplier (19) installed outside via an opening/shutting valve (20) through a filter (21) equipped in a load lock chamber (4). The filter (21) may have many fine pores as same as those in the shower head for gas or may be a porous substance made into fine sintered product.

At the bottom of the load lock chamber (4), there is provided an exhaust (2) such as a turbomolecular pump and a rotary pump via an exhaust opening (22) and a valve (23). By this exhaust (24), the load lock chamber (4) is exhausted from

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atmospheric pressure to a predetermined degree of vacuum such as from several tens hPa to 1×10^{-5} hPa.

The treating container (50) of the load lock chamber (4) is made of metal material such as aluminum alloy (e.g. Al-Mg alloy). Inner wall of the treating container (50) is usually polished and then an oxidized passivated layer or a fluorinated passivated layer is formed thereon or coated with other materials such as SiO_2, SiC or SiN so that its corrosion, release of gas from the wall and separation of heavy metal from the wall are prevented.

The load lock chamber (4) constituted as above and the joint (7) are installed in a connectable manner via a gate valve (6) and, in the joint (7), a receiving container (2) is installed in a connectable manner.

In a gate valve (6) installed at the side wall of the load lock chamber (4), there is installed a joint (7) which is a path being able to join the door (8) installed at the receiving container (2). In this joint (7), there is installed a space as a path whereby the conveyer (17) in the load lock chamber (4) is able to carry and convey the substrate (11). The joint (7) is constituted in an air-tight manner so that a connecting-through space formed to the receiving chamber (2) formed by opening the gate valve (6) and the door (8) is isolated from outside whereby an air-tight clean space is formed. This joint (7) is constituted in such a manner that inert gas such

as nitrogen and argon or clean air is supplied. The immobile part of the joint (7) is made for a metal material such as an aluminum alloy, e.g. an Al-Mg alloy. Inner wall of the joint (7) is usually polished and then an oxidized passivated layer or a fluorinated passivated layer is formed thereon or coated with other materials such as SiO_2, SiC or SiN.

The receiving container (2) has an air-tight structure and, in its inner side, there are provided a cassette (25) which is able to receive plural substrates (11) and a holder (26) to hold them. The receiving container (2), the cassette (25) and the holder (26) are made of a metal material such as aluminum alloy, e.g. an Al-Mg alloy. Inner wall of them and surface of jig are usually polished and then an oxidized passivated layer or a fluorinated passivated layer is formed thereon or coated with other materials such as SiO_2, SiC or SiN so that their corrosion, release of gas or separation of heavy metal are prevented.

On a side wall of a receiving container (2) such as a side wall surface, there is provided a door (8) which is able to be opened and closed and has an air-tight function in a closed state. The receiving container (2) is in such a structure that, being separated from a semiconductor treating apparatus (1), it is able to convey keeping the inner atmosphere and cleanliness. In the receiving container (2), it may be either in an ordinary pressure (around 1013hPa) filled with inert gas such as nitrogen

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and argon or clean air or in a reduced pressure state by such a gas during the conveyance of this container (2).

On the upper part of the receiving container (2), an opening/shutting valve (28) having an opening (27) is connected to a filter (29) in the receiving container (2) by a pipe. The opening/shutting valve (28) is opened only when inert gas such as nitrogen and argon or clean air is supplied into a receiving container (2) by an outer gas-supplying means such as the gas-supplier (19). At the lower part of the receiving container (2), a valve (31) is connected via an exhaust opening (30) and the valve (31) has an opening (32). The valve (31) is opened only when the receiving container (2) is vacuum exhausted. The vacuum exhaustion is constituted in such a manner that it takes place when an exhaust independently installed outside such as an exhaust (24) is connected to an opening (32).

Operation of this receiving container (2) will be explained. The door (8) of the receiving container (2) which receives plural untreated substrates (11) is closed to give an air-tight state. The inner part of the receiving container (2) is exhausted to an extent of desired degree of vacuum and inert gas such as nitrogen and argon or clean air is introduced thereinto so as to maintain a predetermined degree of vacuum.

Operation of the conveying system for the substrate (11) constituted as above will be explained. The receiving container (2) having a cassette (25) wherein plural substrates (11) are

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received is conveyed by an automatic conveying robot keeping its inner degree of cleanliness at class 1 for example by closing the door (8) and then located next to the joint (7) installed adjacent to the load lock chamber (4) of the semiconductor treating apparatus (1).

The atmosphere in the load lock chamber (4) is vacuum exhausted by an exhaust (24), the opening/closing valve (23) is closed and then inert gas such as nitrogen and argon or clean air is supplied into a load lock chamber (4) from a gas-supplying means (19) until the predetermined pressure is achieved. The gate valve (6) and the door (8) are opened, the load lock chamber (4) and the receiving container (2) are connected and the inner part is made an atmosphere of common inert gas such as nitrogen and argon or clean air. After that, the conveyer (17) in the load lock chamber (4) moves and the substrates (11) are taken out from the cassette (25) in the receiving container (2) and conveyed into a load lock chamber (4).

Then the gate valve (6) is closed and the inside of the load lock chamber (4) is vacuum exhausted to a predetermined degree of vacuum such as 1×10^{-3} hPa. After that, the gate valve (5) is opened and the substrates (11) held by the conveyer (15) are transferred onto the stand (10) in the treating chamber (3).

After the conveyer (17) is escaped into the load lock chamber (4), the gate valve is closed and the inside of the

treating chamber (3) is vacuum exhausted to a predetermined

degree of vacuum. Then predetermined processes such as

supplying of process gas into a treating chamber (3), heating

and generation of plasma are carried out to the substrates (11).

The inside of the treating chamber (3) after completion

of the processes is vacuum exhausted and substituted with

atmosphere of inert gas such as nitrogen and argon or clean

air, the gate valve (5) is opened and the substrates (11) are

conveyed out into the load lock chamber (4) by the conveyer

(17).

After that, the gate valve (5) is closed, the inside of

the load lock chamber (4) is substituted with atmosphere of

inert gas such as nitrogen and argon or clean air, the gate

valve (5) is opened and the substrates (11) are returned to

the predetermined slot of the cassette (25) hold in the receiving

container (2). The conveying system for the substrate (11)

works as such and, when such an operation is repeated by taking

out from the cassette (25) for every single-wafer whereupon

the treatment for all substrates (11) in the cassette (25) is

carried out.

When such a series of treatment is finished, the gate

valve (6) is closed, the semiconductor treating apparatus (1)

is returned to an air-tight state and, at the same time, the

door (8) of the receiving container (2) is closed whereupon

the receiving container (2) is kept in an air-tight atmosphere

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of inert gas such as nitrogen and argon or clean air.

After that, the receiving container (2) in which plural treated substrates (11) are received is conveyed to the semiconductor manufacturing apparatus or a semiconductor testing apparatus of the next step keeping the atmosphere of inert gas such as nitrogen and argon or clean air.

Except when the treatment for the semiconductor substrate is carried out, the conveying system for the substrate, which is operated as above, is always kept in an atmosphere of inert gas such as nitrogen and argon or clean air. As a result, the substrate can be protected from trash, dust and contamination from an outer environment throughout whole steps and, in addition, it is possible to carry out a series of treatments where conveying of the substrate having an effect of shielding the heavy metal contamination can be carried out.

In a surface treating system shown by Fig. 12, only one treating chamber (3) is connected to the load lock chamber (4) although a system where plural treating chambers (3) are connected to the load lock chamber (4) for carrying out plural kinds of treatments are successively carried out to the semiconductor substrate may be acceptable as well. Further, the pressure in the receiving container (2) may be set at that which is optimum for the treatment and, for example, it is made vacuum exhausted by an inert gas such as nitrogen and argon or clean air atmosphere to make it as same as the pressure in

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the load lock chamber (4) which is to be connected such as 1 × 10^{-3} hPa and then conveyed.

On the contrary, it is also possible that the atmosphere of inert gas such as nitrogen and argon or clean air is made higher than the atmospheric pressure to prevent its contamination of outer air into the receiving container (3) and, prior to connection to the load lock chamber (4), this receiving container (2) is made vacuum exhausted to make near the atmospheric pressure followed by connecting to the load lock chamber (4).

Although a shower head (12) was used for supplying the process gas to the treating container (9), it is also possible to install one or more supplying opening(s) in a form of a nozzle. In that case, it is necessary to install an upper electrode instead of a shower head (12) for application of microwave.

Further, in order to promote a dissociation of oxywater, an irradiating function for electromagnetic field of energy of 0.4 eV or more may be installed in the treating chamber (3).

The water for the treatment may be not only light water (H_2O) but also heavy water (D_2O or HDO). Especially when heavy water is used, there is an improvement in electric reliability after carrying out various treatments for oxide film such as suppression of interfacial states generation caused by hydrogen (H) under electric stress.

When a dry cleaning treatment for metal contamination

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such as Al, Cu, Fe or Ni is carried out, it is preferred to use not only a gas containing hydrogen peroxide and water but also other gas together therewith. That utilizes the fact that, as a formation of metal oxide, the reactivity of metal with other gas such as hydrogen fluoride is enhanced.

For example, when a gas containing hydrogen peroxide and water and a reactive gas containing halogen or a chelating agent forming a chelate compound with metal are simultaneously, alternately or continuously supplied to and treated in a treating chamber (3), a metal compound having a relatively high vapor pressure such as metal halide, metal halide oxide, metal chelate compound and metal oxide chelate compound is produced and, therefore, metal contamination can be removed. Examples of the halogen-containing reactive gas are anhydrous hydrogen fluoride, anhydrous hydrogen chloride, anhydrous hydrogen bromide, anhydrous hydrogen iodide, F_2, Cl_2, Br_2, I_2, ClF_3, NF_3, BF_3, BCl_3, BBr_3, BI_3, CF_3Cl, CF_3Br and CF_3I. However, in view of prevention of ozone depletion, it is preferred that the use of a gas containing Cl is to be avoided if at all possible.

When a metal compound having a high vapor pressure is hardly formed such as in the case of Cu, it is preferred to carry out a physical removal means such as to irradiate solid rare gas, solid carbon dioxide, solid alcohol, ice or the like, to apply ultrasonic wave and/or to elevate the temperature. Especially when the above-mentioned metal compound formation

and removing physically are repeated simultaneously, alternately or continuously once or more, it is possible to remove metal contamination such as Cu. In case ultrasonic vibration is applied, transmission efficiency of the ultrasonic wave can be enhanced when vapor of organic solvent wherein vapor pressure under ordinary state is well high and whereby drying of the substrate (11) quickly proceeds such as isopropyl alcohol is supplied to a treating chamber (3) followed by treating or when the treating chamber (3) is made in such a structure that the substrate (11) is able to be dipped in a liquid solvent followed by treating therein.

Further, as mentioned already, in order to suppress the dispersion of endothermic energy generated by adsorption of water with hydrogen peroxide due to collision of molecules, it is first of all important that the total pressure in the treating chamber (3) is low and the exhausting speed is high or, in other words, residence time of the process gas in the treating chamber (3) is short. Second important thing is that vibrational degree of freedom $(3N - 6)$ (where N means numbers of the constituting atoms for a gas molecule) of the gas used for dilution is small or molecular weight of the gas used for dilution is large. The most preferred gas is a heavy rare gas (such as Kr and Xe) where vibrational degree of freedom is zero although diatomic molecule such as nitrogen or oxygen where the vibrational degree of freedom is 1 is preferred as well.

Alcohol such as isopropyl alcohol quickly dries away on the substrate (11) and, therefore, it may be utilized as a gas for dilution but its vibrational degree of freedom is 30. When vibrational degree of freedom is 60 or less, such a substance including isopropyl alcohol dimer can be utilized.

Examples of the present invention will be mentioned as hereunder.

Example 1.

According to a method as shown below, metal contamination on the surface of a semiconductor substrate (11) was subjected to a dry cleaning treatment using a surface treating system shown in Fig. 12.

First, a p-type (100) silicon substrate (11) was dipped into a solution containing Fe so that its surface was intentionally contaminated. When the initial contamination concentration was analyzed by means of a vapor phase analysis of the flameless atomic absorption spectrometry, 1.5×10^{15} atoms/cm^2 of Cu and 5×10^{15} atoms/cm^2 of Fe were detected.

The substrate (11) was placed on a stand (10) in the treating chamber (3), mixed gas of hydrogen peroxide and water in a molar ratio of 1:3 and anhydrous hydrogen fluoride gas in the total pressure of 6.65 hPa were alternately introduced into the treating chamber (3) and microwave of 15 GHz was applied to carry out a cleaning treatment at ambient temperature. Further, a step of irradiation of solid carbon dioxide onto

the surface to be treated of the substrate (11) was carried out for ten cycles where one cycle consisted of 10 seconds.

After that, the substrate (11) was taken out and the residual contamination concentration was determined whereupon the contamination was removed to such an extent that 7×10^9 atoms/cm^2 of Cu and 9×10^9 atoms/cm^2 of Fe were detected.

Example 2.

According to a method as shown below, organic contamination on the surface of a semiconductor substrate (11) was subjected to a dry cleaning treatment using a surface treating system shown in Fig. 12.

First, a positive resist of a novolac type was spin-coated on the surface of silicon substrate (11). After the substrate (11) was placed on a stand (10) in the treating chamber (3), mixed gas of hydrogen peroxide and water in a molar ratio of 1:3 in total pressure of 6.65 hPa was introduced into the treating chamber (3) and microwave of 15 GHz was applied to carry out a cleaning treatment at ambient temperature. This cleaning treatment step was carried out for from 1 to 150 cycle(s) where one cycle consisted of three seconds.

After that, the substrate (11) was taken out from the treating chamber (3) and the resist removal rate was measured. The resist removal rate was 600 nm/min.

Then a positive resist of a novolac type was spin-coated on the above-treated silicon substrate (11). The substrate

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(11) was placed on a stand (10) in the treating chamber (3),
hydrogen peroxide gas and steam were alternately introduced
into the treating chamber (3) to make their molar ratio 1:3
in the total pressure of 6.65 hPa and a cleaning treatment was
carried out under ultraviolet-ray irradiation from a low voltage
mercury lamp together with application of microwave of 15 GHz
at ambient temperature. This cleaning treatment step was
carried out for five cycles where one cycle consisted of three
seconds.

After that, the substrate (11) was taken out and the
residual organic contamination was measured. The carbon
residual contamination concentration can be removed to the
detection limit or less upon measurement by an X-ray
photoelectron spectroscopic method.

Example 3.

According to a method as shown below, particle removal
was carried out by applying a dry cleaning treatment onto the
surface of a semiconductor substrate (11) using a surface
treating system shown in Fig. 12.

First, fine particles of polystyrene were sprinkled onto
the surface of the silicone substrate (11) so that the surface
was intentionally contaminated. After the substrate (11) was
placed on a stand (10) in the treating chamber (3), mixed gas
of hydrogen peroxide and water in a molar ratio of 1:3 in total
pressure of 6.65 hPa was introduced into the treating chamber

(3) and microwave of 15 GHz was applied to carry out a cleaning treatment at ambient temperature. This cleaning treatment step was carried out for from 1 to 50 cycle(s) where one cycle consisted of three seconds.

After that, the substrate (11) was taken out and the removal rate of the particles having 0.1 micron in diameter or more was measured. Organic contamination forming a glue layer which adheres the particles to the substrate (11) was easily oxidized and removed by an oxidizing species derived from hydrogen peroxide and, unlike the liquid phase step, charge of the particles was suppressed and, accordingly, even by a treatment of about 10 cycles, particle removal rate of 98% or more was able to be achieved. When fine particles of silica or fine particles of silicon nitride were sprinkled instead of polystyrene, particle removal rate of 97% or more can be achieved too under the same condition.

Example 4.

According to a method as shown below, silicon oxide film was formed on the surface of semiconductor substrate (11) using a surface treating system shown in Fig. 12.

First, a silicon substrate (11) wherefrom natural oxide film was removed was placed on a stand (10) in the treating chamber (3). Then, a mixed gas of hydrogen peroxide and water in a molar ratio of 1:3 was introduced into the treating chamber (3) in the total pressure of 6.65 hPa, microwave of 15 GHz was

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applied and an oxidation treatment was carried out at 600°C for 500 minutes.

After that, the substrate (11) was taken out and the characterization of the formed silicon oxide film was carried out. Refractive index was 1.46, thickness of the oxide film was 4 nm, interfacial states density was $1 \times 10^{10}/cm^2$, leak current upon application of 5 MV/cm was 2×10^{-10} A/cm^2 and defect density as measured by an electron spin resonance method was not more than the detection limit for all of E' center, Pb center, peroxy radical and non-bridging oxygen hole center. Thus, the same or more electrical properties were achieved as compared with the oxide film formed by the use of conventional dry oxide film or reactive oxygen such as oxygen atom and its exited states.

Example 5.

According to a method as shown below, the so-called pretreatment, i.e. a dry cleaning treatment, and a silicon oxide film forming treatment was sequentially carried out using a surface treating system shown in Fig. 12. Incidentally, this dry cleaning treatment is to remove the metal contamination, organic contamination and particles on the surface of the substrate (11).

First, a silicon substrate (11) wherefrom natural oxide film was removed was placed on a stand (10) in the treating chamber (3). Then, a mixed gas of hydrogen peroxide and water in a molar ratio of 1:3 was introduced into the treating chamber

(3) in the total pressure of 6.65 hPa and cleaning treatment where ultraviolet ray irradiation from a low-voltage mercury lamp was applied together with application of microwave of 15 GHz at ambient temperature was carried out. This cleaning treatment step was carried out for five cycles where each cycle consisted of three minutes.

Then a mixed gas of hydrogen peroxide and water in a molar ratio of 1:3 and anhydrous hydrogen fluoride were alternately introduced thereinto in the total pressure of 6.65 hPa, a cleaning treatment was carried out by applying microwave of 15 GHz at ambient temperature and then solid isopropyl alcohol was irradiated to the substrate (11). Such a cycle was carried out for ten cycles wherein one cycle consisted of ten seconds.

Further, a mixed gas of hydrogen peroxide and water in a molar ratio of 1:3 was introduced into the treating chamber (3) in the total pressure of 6.65 hPa, microwave of 15 GHz was applied and an oxidation treatment was carried out at 600°C for 500 minutes.

After that, the substrate (11) was taken out and the characterization of the formed silicon oxide film was carried out. Refractive index was 1.46, thickness of the oxide film was 4 nm, interfacial states density was $9 \times 10^9/cm^2$, leakage current at 5 MV/cm was 1×10^{-10} A/cm^2 and defect density as measured by an electron spin resonance method was not more than the detection limit for all of E' center, Pb center, peroxy

radical and non-bridging oxygen hole center. Thus, the same or more electrical properties were achieved as compared with the oxide film formed by the use of conventional dry oxide film or reactive oxygen such as oxygen atom and its exited states and also as compared with the case of Example 4 where a silicon oxide film forming treatment was solely carried out. Incidentally, this sequential treatment may be carried out in the same treating chamber or by conveying the substrate (11) to be treated to another treating chamber or to another treating apparatus.

Example 6.

According to a method as shown below, a silicon oxide film forming treatment using heavy water was carried out using a surface treating system shown in Fig. 12.

First, a silicon substrate (11) wherefrom natural oxide film was removed was placed on a stand (10) in the treating chamber (3). Then, a mixed gas of hydrogen peroxide and heavy water (D_2O) in a molar ratio of 1:3 was introduced into the treating chamber (3) in the total pressure of 6.65 hPa and an oxidation treatment was carried out by application of microwave of 15 GHz at 600°C for 500 minutes.

After that, the substrate (11) was taken out and the characterization of the formed silicon oxide film was carried out. With regard to an oxide film of as grown, concentration of the contained heavy water was 1×10^{19} atoms/cm^3, refractive

index was 1.46, thickness of the oxide film was 4 nm, interfacial states density was $1 \times 10^{10}/cm^2$, leakage current at 5 MV/cm was 2×10^{-10} A/cm^2 and defect density as measured by an electron spin resonance method was not more than the detection limit for all of E' center, Pb center, peroxy radical and non-bridging oxygen hole center. Thus, the same result as in Example 4 where light water (H_2O) was used was achieved.

However, an increase in the interfacial states density after application of an F-N stress up to 10C/cm^2 under the charge injection condition of Jg = -0.01 A/cm^2 was suppressed to an extent of about 60% as compared with Example 4. In addition, dispersion of the interfacial states density after application of an F-N stress was significantly decreased as compared with the case of light water.

Example 7.

According to a method as shown below, a thermal treatment of a metal oxide was carried out using a surface treating system shown in Fig. 12.

First, a thermodynamically stable SrTiO$_3$ layer was formed on a TiAlN barrier layer made on one of the main surfaces of a silicon substrate (11) and then a metal oxide film capacitor in a structure of SrRuO$_3$/BaTiO$_3$/SrRuO$_3$ was formed.

After that, the silicon substrate (11) was placed on the stand (10) in the treating chamber (3). Further, a mixed gas of hydrogen peroxide and water in a molar ratio of 1:3 was

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introduced into the treating chamber (3) in the total pressure of 6.65 hPa, microwave of 15 GHz was applied and an oxidizing treatment was carried out at 600°C for 90 minutes.

In this oxidizing treatment, neither film peeling nor swelling that occurs in a vacuum thermal treatment was noted. The c-axis length of the $BaTiO_3$ ferroelectric layer as measured by an X-ray diffraction method showed an elongation of as long as 0.414 nm. Ferroelectric characteristic was as good as 60 mC/cm^2 when the ferroelectric film thickness was about 30 nm and applied voltage was 1 V. In addition, the squareness ratio of hysteresis was improved whereby an operation under lower voltage was possible. Further, an imprint in the initial state was less than the case where the electrode was sandwiched with platinum and a vacuum thermal treatment was carried out at 1.33 $\times$ 10^{-6} hPa.

Example 8.

According to a method as shown below, a chemical vapor-phase deposition (CVD) treatment of a fluorine-added silicon oxide film was carried out using a surface treating system shown in Fig. 12.

First, a silicon substrate (11) wherefrom natural oxide film was removed was placed on a stand (10) in the treating chamber (3), a mixed gas of hydrogen peroxide and water in a molar ratio of 1:3, SiF_4 gas and SiH_4 gas were introduced into the treating chamber (3) at the flow rates of 500 cm^3/minute,

50 cm^3/minute and 20 cm^3/minute, respectively until the total pressure became 6.65 hPa, microwaves of 15 GHz and 13.56 GHz were applied to the upper electrodes while RF bias of 13.56 MHz was applied to the lower electrode at 470°C to form a fluorine-added silicon oxide film.

After that, the substrate (11) was taken out and the characteristics of the resulting fluorine-added silicon oxide film were investigated. The fluorine-added silicon oxide film was a low-dielectric film where fluorine concentration was 12 at%, refractive index was 1.36 and dielectric constant was 3.4. After the substrate (11) was exposed for one week to an atmospheric environment in a clean room, neither H_2O nor Si-OH was detected by FT-IR, SIMS, and TDS measurement. It was possible to form a low dielectric fluorine-added silicon oxide film having good moisture resistance.

With regard to a defect density measured by an electron spin resonance method, E' center was $3 \times 10^{-16}/cm^3$ and the defect assigned as peroxy radical and non-bridging oxygen hole center was $1 \times 10^{16}/cm^3$ which were found to be smaller than the conventional plasma CVD oxide film. Incidentally, unless fluorine-containing gas such as SiF_4 is introduced, normal silicon oxide film is formed. In addition, TEOS ($Si(OC_2H_5)_4$) and fluorinated gas thereof ($SiF_n(OC_2H_5)_{4-n}$, $n = 1-3$), fluorinated silane gas SiF_nH_{4-n}, etc. used for formation of fluorine-containing silicon oxide film and silicon oxide film

may be used as well.

As illustrated hereinabove, in the present invention, a cluster where the first and the second molecules are bonded by means of an intermolecular force is formed and, therefore, it is possible that first molecule is made more reactive in a very efficient manner. Accordingly, in accordance with the present invention, a surface treating at a sufficient processing rate is possible. Further, in the present invention, hydrogen oxide molecule and water molecule for example can be used as the first and the second molecules, respectively and the surface of the member can be treated using oxywater. Thus, according to the method of the present invention, it is possible to carry out a surface treating using chemical substances that need no additional environmental management even if exhausted into environment. Furthermore, in the present invention, the surface treating of the member is carried out in a gas phase. Thus, unlike in the case of carrying out it in a liquid phase, the surface treating can be done without the use of a large amount of pure water as a solvent or a rinse agent.

Thus, in accordance with the present invention, there is provided a surface treating method with a small environmental load. Further, there is provided a surface treating method in which a surface treating is possible by a sufficient processing rate. Furthermore, there is provided a surface treating method in which a surface treating is possible without

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the use of large amount of pure water.